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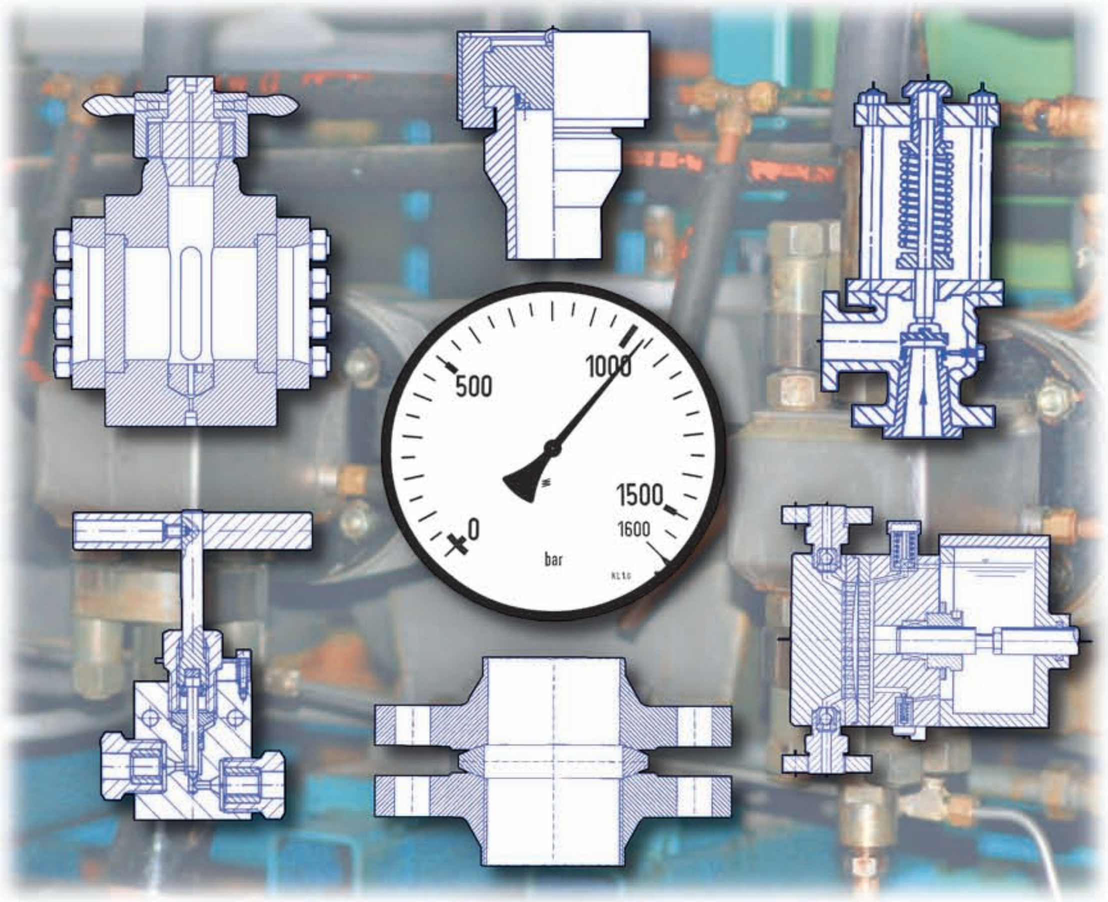
Processes, Equipment and Safety



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Preface

In 2010, when Wiley-VCH Verlag GmbH asked me to edit a new book on high-pressure applications, the first thought that came to my mind was whether there was really a requirement for compiling such a reference book. In fact, numerous conference proceedings and even some textbooks were available that illustrated the state of the art and special applications of high-pressure processes in detail, offering support for production of innovative products. However, the application of high pressure covers many different industries – from basic material production, mechanical engineering, energy management, chemical engineering to bioprocessing and food processing. In engineering education, these applications even postulate different courses of study.

Based on this background, it is not surprising that a general and comprehensive description of industrial high-pressure processes is hardly possible. Next to basic knowledge, the aim was now to especially include overall aspects such as the need for applying high pressure, desirable and undesirable effects, and prospects and risks of high-pressure processes. In this respect, my activities on high-pressure engineering in industry and university since 1977 facilitated access to experts from various different fields of industrial applications and scientific research who were willing to contribute with their knowledge to special high-pressure applications.

The book is structured in three main parts. Part One is an introductory section dealing with the history and the engineering basics of high-pressure techniques. Part Two demonstrates classical and more recent high-pressure applications from chemical engineering, energy management and technology, bioengineering and food engineering, and manufacturing techniques. Part Three concentrated on equipment, measurement, and safety devices in high-pressure processes. The book concludes with a short survey and an evaluation of international rules that are valid for the calculation and design of high-pressure vessels.

It is my pleasure to thank all the authors for their commitment and their highly valuable and professional contributions. I also thank Wiley-VCH Verlag GmbH for consistent assistance and patience.

Hamburg, June 2012 *Rudolf Eggers*

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Part One
Introduction

Industrial High Pressure Applications: Processes, Equipment and Safety, First Edition. Edited by Rudolf Eggers.

1
Historical Retrospect on High-Pressure Processes

Rudolf Eggers

The historical development of high-pressure processes since the beginning of the industrial period is based on two concepts: first, the transfer of the inner energy of water vapor at elevated pressures into kinetic energy by the invention of the steam engine; second, the movement of gas-phase reaction equilibrium at high pressures enabling the production of synthetic products like ammonia. Thus, the industrial use of high-pressure processes goes back to both mechanical and chemical engineering. Beginning in the second half of the eighteenth century, the need of safe and gas-tight steam vessels up to few megapascals became essential because that time many accidents happened by bursting of pressure vessels. Chemical industry started high-pressure synthesis processes in the early twentieth century. Compared to moderate working pressures of steam engines, the pressure range now was extremely high between 10 and 70 MPa. As a consequence, a fast growing requirement for high-pressure components like high-pressure pumps, compressors, heat transfer devices, tubes and fittings, reliable sealing systems, and in particular new pressure vessel constructions developed.

Besides, mechanical and chemical engineering material science has promoted the development of new high-pressure processes by creating high ductile steels with suitable strength parameter.

Finally, the safety of high-pressure plants is of outstanding importance. Thus, in the course of development, national safety rules for vessels, pipes, and valves have been introduced by special organizations. For example, in 1884, the American Society of Mechanical Engineering (ASME) launched its first standard for the uniformity of testing methods of boilers. The German society TÜV was founded in 1869 in order to avoid the devastating explosions of steam vessels.

The following list of year dates shows essential milestones of high-pressure processes concerning their development and technical design:

1680: Papins construction of the first autoclave for evaporating water. The design shows the idea of an early safety valve working on an adjustable counterbalance.
1769: James Watt introduced the steam engine transferring thermal energy in motive power.

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1826: Jacob Perkins demonstrated the compressibility of water by experiments above 10 Mpa. Caused by the increasing application of steam engines, the boiling curve of different media became of interest. It was observed that boiling temperatures increase with rising pressure. That time one assumes a remaining coexistence of liquid and gas phase up to any high pressure. It was the Irish physicist and chemist Thomas Andrews who in 1860 disproved this assumption. On the basis of experiments with carbon dioxide, he was able to demonstrate a thermodynamic state with no difference between liquid and gas phase characterized by a distinct value of temperature, pressure, and density. This point has been called the "critical point."

1852: J.P. Joule and W. Thompson discovered the cooling effect caused by the expansion of gases during pressure release.

1873: J.D. van der Waals gives a plausible explanation for the behavior of fluids at supercritical condition.

1900: W. Ostwald claimed a patent on the generation of ammonia by the combination of free nitrogen and hydrogen in the presence of contacting substances.

1913: F. Haber and C. Bosch: First commercial plant synthesizing ammonia from nitrogen and hydrogen at 20 Mpa and 550 °C. The reactors were sized at an inner diameter of 300 mm and a length of 8 m. The productivity of one reactor was 5 ton/day [1]. The pressure vessel was equipped with an in-line tube made from soft iron and degassing holes in order to protect the pressure-resistant walls against hydrogen embrittlement. This process was the forerunner of many others that have been developed into commercial processes [2].

1920: First application of methanol synthesis as a conversion of carbon monoxide and hydrogen at a pressure of 31 MPa and temperatures between 300 and 340 °C.

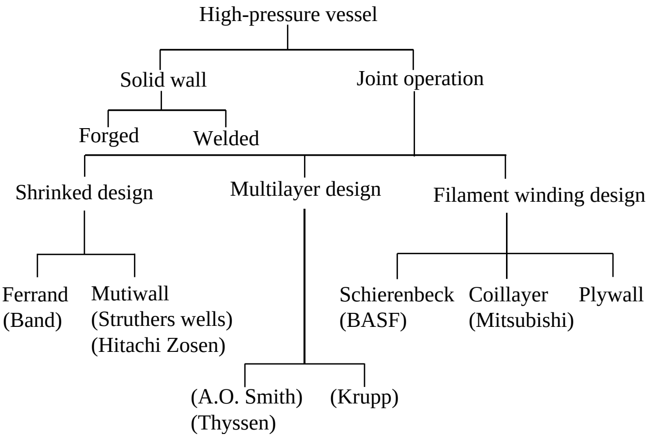

Figure 1.1 Survey on high-pressure vessel design [3].

1924: First industrial plant for direct hydrolysis of fuel from coal at 70 MPa based on the Bergius process, which was claimed at 1913.
1953: Initiation of a polyethylene production at about 250 MPa.
1978: First commercial decaffeination plant using supercritical carbon dioxide as a solvent.

The development of high-pressure vessel design is characterized by the initiation of seamless and forged cylindrical components. The two versions are the forged solid wall construction and a group of different layered wall constructions. Among these, the BASF Schierenbeck vessel plays an important role, because these vessels are manufactured without welding joints. Figure 1.1 presents an overview.

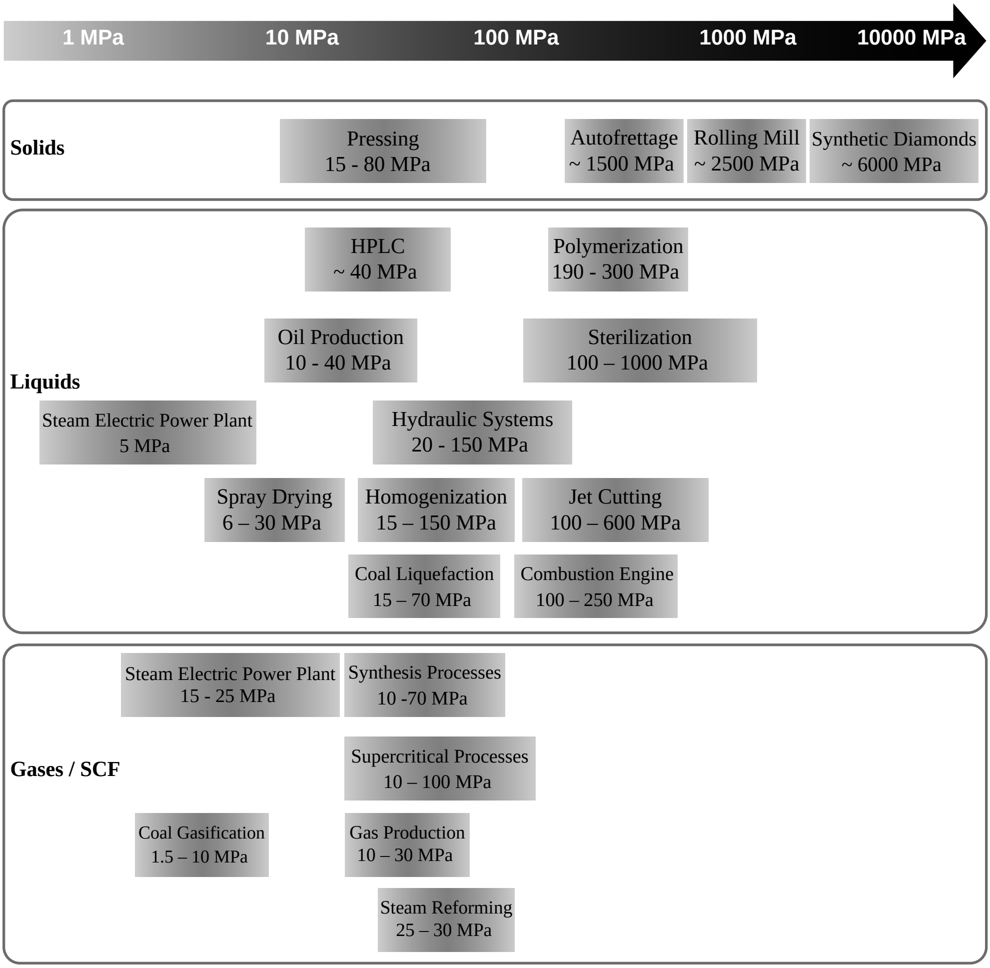

Figure 1.2 Working pressures of currently used high-pressure processes.

Special high-pressure closures have been developed equipped with single or double tapered sealing areas. A breakthrough toward leak-tight high-pressure devices was without doubt the "principle of the unsupported area" from Bridgman [2]. His idea extended the accessibility of pressures up to 10 000 MPa. Another concept is that the metallic lens ring enabled safe connections of high-pressure tubes and fittings.

Up to now new high-pressure processes have been introduced constantly. Materials like ceramics, polymers, or crystals having special properties are generated and formed in high-pressure processes. The current increase in liquid natural gas (LNG) plants is not possible with safe high-pressure systems. Also, the enhanced recovery of oil and gas by fluid injection at very high pressures requires qualified compressors, tubes, and safety valves. High-pressure fuel injection decreases the efficiency of combustion engines.

An example of current development is the investigation of processes aiming homogenization and even sterilization in industrial scale at high pressures up to 1000 MPa. Figure 1.2 illustrates the pressure regimes of currently operated high-pressure processes.

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2 Spain, I.L. and Paauwe, J. (eds.) (1977) *High Pressure Technology*, vol. I, Marcel Dekker Inc., New York.

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2

Basic Engineering Aspects

Rudolf Eggers

2.1

What are the Specifics of High-Pressure Processes?

It is obvious that with increasing process pressure, the distances between molecules of solid, liquid, or gaseous systems become smaller. Generally, such diminishing of distances results in alterations of both the phase behavior of the system and the transport effects of the considered process. Consequently, in designing the high-pressure processes, not only the knowledge of phase equilibrium data for pure and heterogeneous systems is needed from thermodynamics but also the reliable data for material and transport properties at high pressures are of high importance, because these can fluctuate strongly especially in the near-critical region of a medium.

In Figure 2.1, an easily interpreted image illustrates the molecule distances depending on pressure and temperature. The three phases – solid, liquid, and gas – are differentiated by the phase transition lines for melting, evaporation, and sublimation. At the critical point, the processes of condensation and evaporation merge.

Besides the decreasing molecule distances at enhanced pressures, the diagram reveals the continuous transfer from the gas phase into the liquid region by passing the so-called supercritical region without any crossing of a phase change line. Because this region is connecting the low-density region of gas and the high-density region of liquid state, it is evident that the corresponding density gradients without phase change are highest in the near-critical region. As a consequence, high pressure enables the use of fluid phases as solvents with liquid-like densities and gas-like diffusivities. Table 2.1 exemplifies that the basic engineering aspects of high-pressure processes are based on phase equilibrium data and material properties for both single and multicomponent systems and further they will be influenced by relevant transport data.

Of course, plant engineering and vessel design are also basic aspects of high-pressure processes. Due to their significance in industrial applications of high-pressure processes, these aspects are discussed in Chapter 12. Nevertheless,

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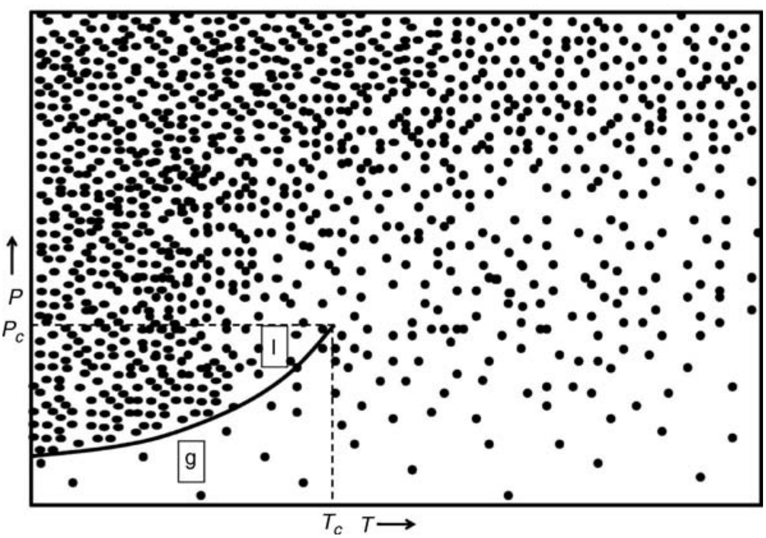
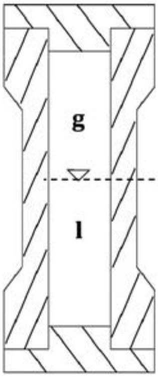


Figure 2.1 Molecule distances dependent on pressure and temperature.

this chapter focuses on the thermodynamic aspects of high-pressure phase equilibrium and the influence of pressure on material and transport data for heat and mass transfer at high pressures, including some information on basic measuring principles, which are given in detail in Chapter 14.

Table 2.1 High-pressure phase equilibrium: material properties and transport data in corresponding phase state.



Density	Viscosity	Diffusivity	Interfacial tension
liquid like	gas like	between gas and liquid	reduced in case of partial miscibility impact on wettability
liquid	strongly reduced	enhanced	

2.2
Thermodynamic Aspects: Phase Equilibrium

In many industrial high-pressure processes, the involved mass flows are getting in direct contact in order to enable heat and mass transport. The well-known examples are extraction processes using supercritical fluids (see Chapter 8) or liquefying processes of gas mixtures under pressure in combination with transport and storage of natural gas [1]. Further examples are the carbon capture and storage technology (CCS) (see Chapter 6), enhanced oil recovery processes (see Chapter 7), refrigeration cycles, and renewable energy processes (see Chapter 10).

Transport processes across phase boundaries of contacting phases are controlled by driving gradients of pressure, temperature, and chemical potential of each component inside a phase as long as phase equilibrium is not established and these gradients are existing. A phase is defined as a homogeneous region without discontinuities in pressure, temperature, and concentration. Thus, phase equilibrium is accomplished when the corresponding phases are of the same pressure (mechanical equilibrium), of the same temperature (thermal equilibrium), and of the same chemical potential (material equilibrium) for each component the system contains [2]. The chemical potential of a single component represents the change of internal energy of a system when the molar mass of this component varies. Instead of using the relative inaccessible chemical potential, it is possible to equalize the fugacities of the different phases. As the fugacity demonstrates an adjusted pressure considering the forces of interaction between the molecules in a real system, this quantity is of high importance for phase equilibrium especially in heterogeneous high-pressure systems [3]. The Gibbs phase rule predicts the number of degrees of freedom F for a mixture of K coexisting phases and n components:

$$F = 2 - K + n \tag{2.1}$$

The phase equilibrium constitutes a thermodynamic limitation of transfer processes. Therefore, the knowledge of phase equilibrium is an essential precondition for specification and calculation of high-pressure processes.

High-pressure processes need the knowledge of phase equilibrium for pure substances, binary systems, and multicomponent system. Nowadays data of high precision are available for pure components like water [4] and for numerous gases [5, 6] up to very high pressures. These data are computable by empirical equations. So far, the calculation of phase equilibrium for mixtures is recommended by use of equations of state. As such there are modified Redlich–Kwong and Peng–Robinson equations that have been proven for high-pressure systems [3]. Recently, the perturbation theory has attracted increasing research interest [7]. Thus, the so-called PCSAFT equation is established for polymeric systems and further application in high-pressure processing [8].

2.3
Software and Data Collection

For modern industrial engineering, an increasing number of capable software tools have been developed and are commercially available. Some of these are well-known examples that have been proved of value for calculation of high-pressure phase equilibrium: ASPEN PLUS (www.aspentech.com), Simulis Thermodynamics (www.prosim.net), and PE 2000 Phase Equilibrium (www.sciencecentral.com). Furthermore, there are data banks with experimental data for pure components and even multicomponent systems at high pressures (www.ddbst.com). Also, data on material properties are available, for instance, at www.dechema.de or webbook.nist.gov/chemistry. Finally, the well-experienced companies offer experimental determination of unknown data for high-pressure processes.

As an example for high-pressure system properties, Figure 2.2 demonstrates the phase behavior of CO_2 and Figure 2.3 illustrates the different phases of the binary system CO_2–water [9].

2.4
Phase Equilibrium: Experimental Methods and Measuring Devices

Although the direct measurement of equilibrium data for mixtures at high pressures requires detailed experimental experience and expensive equipment, it is still an essential and reliable way in order to obtain the data needed for the evaluation of high-pressure processes. Recently, Dohrn *et al.* [10] presented a classification of experimental methods for high-pressure phase equilibria. Figure 2.4 illustrates the two main groups: analytical methods and synthetic methods. In case of analytical

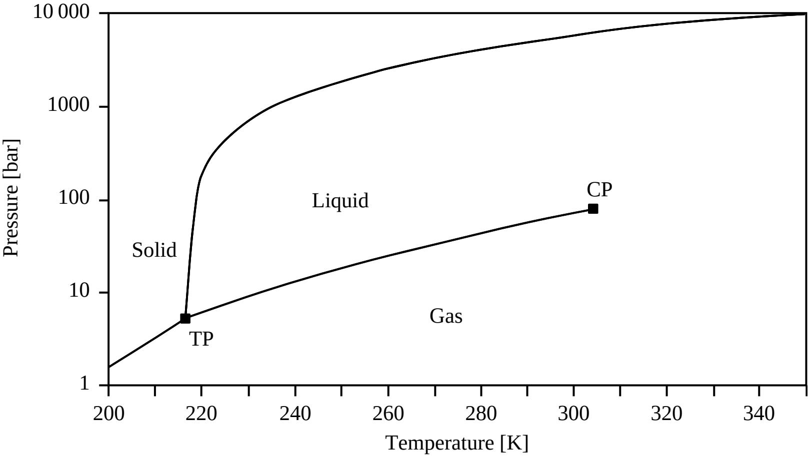


Figure 2.2 p, T diagram for CO_2.